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Angular autocorrelation functions in molecular crystals: Application to nuclear magnetic resonance relaxation and Raman spectra

Bashirov F.
Kazan Federal University, 420008, Kremlevskaya 18, Kazan, Russia

Abstract

The theory of hindered molecular motion (HMM) in crystals, extended by taking the molecular site symmetry into account, is used in the calculation of the angular autocorrelation functions (ACFs). The basic model of motion involves a molecular rearrangement by means of random angular jumps of an intramolecular vector according to a crystallographic point symmetry group G between the potential wells in which the probability density of the vector orientation is continuously distributed over the angles. New physical quantities, the dynamical weights of the irreducible representations of the group G, are introduced to relate the molecular site symmetry in the ACFs. The polycrystalline ACFs are convenient for describing the HMM in liquids. The ACFs of the second-rank unitary spherical tensors are presented in an explicit form for all the point groups of pure rotation. The surface-plot graphs of the ACF amplitude, drawn as functions of a dynamical weight and an angle of crystal orientation, make the features of the HMM description more comprehensible. The new ACFs are applied to processing the exponential magnetic relaxation of the dipole and quadrupole nuclei and the line shape of Raman scattering in molecular crystals. Quantitative data about the NH+ 4-ion motion and its site symmetry are obtained from the anisotropic magnetic spin-lattice relaxation of protons and deuterons in ammonium chloride. The theoretical anisotropy of the Raman line intensities corresponding to the internal vibration modes is in accord with experiment and with the common methods of group-theoretical analysis in the vibration spectroscopy of molecular crystals.